



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 780 421 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
25.06.1997 Bulletin 1997/26

(51) Int. Cl.<sup>6</sup>: **C08J 3/03**  
// C08L83:04

(21) Application number: **96120674.5**

(22) Date of filing: **20.12.1996**

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **21.12.1995 US 576114**

(71) Applicant: **DOW CORNING CORPORATION**  
**Midland, Michigan 48686-0994 (US)**

(72) Inventors:  
• **Hill, Michael Philip Louis**  
**Midland, Michigan 48640 (US)**

• **Tselepis, Arthur James**  
**Midland, Michigan 48640 (US)**  
• **Wolf, Andreas Thomas Franz**  
**Midland, Michigan 48642 (US)**

(74) Representative: **Spott, Gottfried, Dr.**  
**Patentanwälte**  
**Spott, Weinmiller & Partner**  
**Sendlinger-Tor-Platz 11**  
**80336 München (DE)**

**(54) Aqueous silicone emulsions forming silicone elastomers adhering to substrates**

(57) This invention relates to an aqueous silicone emulsion which forms a silicone elastomer upon the removal of water having improved adhesion to substrates. The silicone emulsion comprises the product formed by mixing a diorganosiloxane polymer, water, surfactant, optionally a crosslinker, a tin condensation catalyst, optionally an acid and an effective amount of an aminofunctional siloxane which is formed by reacting an aminofunctional silane and a hydroxy-endblocked organosiloxane.

EP 0 780 421 A2

## Description

This invention relates to an aqueous silicone emulsion which forms a silicone elastomer upon removal of water and has improved adhesion to substrates.

The literature teaches that aqueous silicone emulsions are dispersions of siloxane polymers in water. Crosslinking of siloxane polymers takes place either before or after evaporation of water, although crosslinking prior to water evaporation is more common. Upon water evaporation, silicone emulsions produce silicone elastomers in the form of coatings, sealants and caulks.

Generally, silicone elastomers from aqueous silicone emulsions have excellent resistance to weathering, moderate high temperature stability and good low temperature properties. For these elastomers to have appreciable mechanical properties, reinforcement of the elastomer is required. This reinforcement is achieved by use of various fillers, including colloidal silica, precipitated silica or fumed silica and silica formed in-situ from precursor silicon-containing compounds.

Due to their property profile, silicone elastomers find use as sealants, coatings, caulks and additives widely used in building construction. Other ingredients may also be added depending on the specific use in mind, such as thickeners, rheology modifiers, dispersants, pigments, flattening agents, defoamers, adhesion promoters and freeze-thaw stabilizers.

One disadvantage of silicone elastomer from aqueous silicone emulsions is that they lack good adhesion to substrates. Considerable effort has been devoted to finding ways to improve the adhesion of such silicone elastomers. This prior art is broadly represented by GB-A 2,152,521; JP-A 58/69250; US-As 3,817,894; 4,228,054; 4,412,035; 4,496,687; 4,535,109; 4,710,405 and 4,877,828.

Although the above methods result in better adhesive properties for the silicone elastomer, problems still exist. One problem arises because adding neat aminofunctional silanes to silicone emulsions tend to destabilize the emulsion resulting in poor shelf life, agglomeration or coagulation. In addition, any improvements in adhesion obtained by addition of neat aminofunctional silanes are not maintained over a period of more than 2 to 6 weeks since condensation of the hydrolyzed adhesion promoter causes it to deactivate.

An objective of this invention is to prepare an aqueous silicone emulsion which forms a silicone elastomer upon removal of water having improved adhesion to substrates. Another objective is to prepare such an emulsion, having improved shelf life while in emulsion form, which forms a silicone elastomer upon removal of water. A final objective is to maintain the improvements of shelf life and adhesion over an extended period.

The objectives of this invention are achieved by preparing an aqueous silicone emulsion which forms an elastomer upon the removal of water having an improved adhesion to substrates. This emulsion comprises the product formed by mixing a diorganosiloxane polymer, water, surfactant, optionally a crosslinker, a tin condensation catalyst, an effective amount of an aminofunctional siloxane which is formed by reacting components comprising an aminofunctional silane and a hydroxy-endblocked organosiloxane, and optionally an acid.

This invention is an aqueous silicone emulsion, the silicone emulsion comprising the product formed by mixing:

(A) a diorganosiloxane polymer having the general formula (I)  $X_{3-n}R_n-YO-(R^1_2SiO)_z-Y-R_nX_{3-n}$  where

n is 0, 1, 2 or 3,

z is an integer from 200 to 10,000,

X is a hydroxyl group or hydrolyzable group,

R is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms,

R<sup>1</sup> is individually selected from X groups and R groups, provided, at least 90% of the R<sup>1</sup> groups are R groups, and

Y is a Si atom, a  $-Si-(CH_2)_mSiR^1_2-$  group or a  $-Si-(CH_2)_mSiR^1_2-O-SiR^1_2-(CH_2)_mSiR^1_2-$  group, where R<sup>1</sup> is defined above and m is a positive integer;

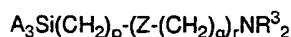
(B) water;

(C) a surfactant;

(D) optionally, a crosslinker;

(E) a tin condensation catalyst;

(F) an effective amount of an aminofunctional siloxane which is formed by reacting components comprising an aminofunctional silane (II) having the formula



where, A is a hydrolyzable group, Z is an oxygen atom or NR<sup>2</sup>, where R<sup>2</sup> is individually selected from hydrogen atom or substituted and unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms, R<sup>3</sup> is also

individually selected from hydrogen atom or substituted and unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms, p and q are each a positive integer from 2 to 10 and r is a positive integer from 0 to 3; and a hydroxy-endblocked organosiloxane (III) having the formula  $\text{HO}-(\text{SiR}^4_2)_b\text{-OH}$  where  $\text{R}^4$  is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms and b is a positive integer from 4 to 80; and  
(G) optionally, an acid.

Component (A) is a diorganosiloxane polymer. The term "diorganosiloxane polymer" as used herein means siloxane compositions having mixtures comprising only a single type of siloxane polymer or mixtures thereof. The diorganosiloxane polymer can also be a homopolymer, copolymer or terpolymer. In addition, the term includes different kinds of molecules, such as long chain linear and branched molecules or short chain linear and branched molecules. Although not critical to this invention, the viscosity of the organosiloxane polymer is in the range of 5,000 to 500,000 mPa · s, and preferably in the range of 10,000 to 100,000 mPa · s. However, higher molecular weight polymers can be used if the viscosity is adjusted using solvent, polymer blending or the like.

The "diorganosiloxane polymers" used herein are well known to those skilled in the art. They are described by formula (I) above and are either commercially available or made by known methods.

Substituent X represents one or more groups bonded to a silicon atom and is either a hydroxyl group or a hydrolyzable group. Hydrolyzable groups include any group attached to silicon that is hydrolyzed by water at room temperature. Suitable groups represented by X include hydrogen atom; halogen atoms such as chlorine, bromine, fluorine or iodine; groups of the formula  $-\text{OT}$  when T is any hydrocarbon or halogenated hydrocarbon group such as methyl, ethyl, isopropyl, octadecyl, allyl, hexenyl, cyclohexyl, phenyl, benzyl, beta-phenylether, 2-chloroethyl, chlorophenyl, 3,3,3-trifluoropropyl and bromocyclohexyl; any hydrocarbon ether radical such as 2-methoxyethyl, 2-ethoxyisopropyl, 2-butoxyisobutyl, p-methoxyphenyl and  $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$ ; any acyl radical such as acetyl, propionyl, benzoyl, cyclohexoyl, acrylyl, methacrylyl, stearyl, naphthoyl, trifluoroacetyl, chlorobenzoyl and bromopropionyl; any acyloxy group such as acetoxyl, benzoyloxy, propionoxyl or acryloxy; and any amino radical such as  $\text{NH}_2$ , dimethylamino, diethylamino, ethylmethylamino, diphenylamino, methylphenylamino or dicyclohexylamino. X can also be any aminoxyl radical of the formula  $-\text{ONT}_2$  or  $-\text{ONT}'$  in which T is as defined above and T' is any divalent hydrocarbon radical both valences of which are attached to the carbon, such as hexylene, pentylen and octylene; any ketomime radical of the formula  $-\text{ON}=\text{CT}_2$  or  $-\text{ON}=\text{CT}'$  in which T and T' are defined above; ureido groups of the formula  $-\text{N}(\text{T})\text{CONT}'_2$  in which T is defined above and T' is hydrogen atom or any of the T radicals; carbamate groups of the formula  $-\text{OOCNTT}'$  in which T and T' are defined above; and carboxylic amide radicals of the formula  $-\text{NTC}=\text{O}(\text{T}')$  in which T and T' are defined above. X can also be the sulfate group or the sulfate ester groups of the formula  $-\text{OSC}_2(\text{OT})$  where T is as defined above; the cyano group; the isocyanate group; and the phosphate or phosphate ester groups of the formula  $-\text{OPO}(\text{OT})_2$  where T is as defined above.

Hydroxyl groups and alkoxy groups are preferred groups for X. Illustrative alkoxy groups are methoxy, ethoxy, propoxy, isobutoxy, pentoxy, hexoxy and 2-ethylhexoxy. The more preferred group for X is the hydroxyl group.

Substituents R and  $\text{R}^1$  each represent substituted or unsubstituted monovalent hydrocarbon groups having from 1-15 carbon atoms bonded to a silicon atom, which may or may not be identical, provided at least 90% of the  $\text{R}^1$  groups are unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms. Examples of suitable substituted or unsubstituted monovalent hydrocarbon radicals of R and  $\text{R}^1$  are alkyl radicals such as methyl, ethyl, isopropyl, hexyl, octadecyl and myrcyl; alkenyl radicals such as vinyl, allyl or hexenyl; alkynyl radicals such as propargyl, cycloaliphatic radicals such as cyclopentyl, cyclohexyl and cyclohexenyl; aromatic hydrocarbons such as phenyl, tolyl, xylyl, xenyl, naphthyl and anthracyl; aralkyl hydrocarbon radicals such as benzyl, beta-phenylethyl, beta-phenylpropyl or gamma-tolylpropyl; and halogenated hydrocarbon or carbon radicals such as 3,3,3-trifluoropropyl, tridecafluoro-1,1,2,2-tetrahydrooctyl-1-methyl or perfluoroalkyl. In addition,  $\text{R}^1$  is an X group.

R and  $\text{R}^1$  are preferably methyl groups or methyl and phenyl groups. More preferably, both R and  $\text{R}^1$  are methyl groups.

Substituent Y represents a single silicon atom or groups which include methylene spacer groups attached to silicon, having the formula  $-\text{Si}-(\text{CH}_2)_m\text{SiR}^1_2-$  or  $-\text{Si}-(\text{CH}_2)_m\text{SiR}^1_2-\text{O}-\text{SiR}^1_2-(\text{CH}_2)_m\text{SiR}^1_2-$ , where  $\text{R}^1$  is defined above and m is a positive integer. Y is more preferably a silicon atom for this invention.

The diorganosiloxane polymers can be present as a mixture of different diorganosiloxane polymers so long as there is on average at least 1.3 hydroxyl or hydrolyzable groups or a mixture thereof, per molecule. Preferably, there is on average at least 1.6 hydroxyl or hydrolyzable groups or a mixture thereof per diorganosiloxane polymer molecule, and most preferably there are at least 2 hydroxyl or hydrolyzable groups or a mixture thereof, per polymer molecule. These diorganosiloxane polymers which are present as a mixture are prepared by mixing the individual diorganosiloxane polymers prior to emulsification or by emulsifying them individually and then mixing the emulsions.

Preferred diorganosiloxane polymers include hydroxyl endblocked PDMS polymers, ethylene trialkoxysilyl endblocked PDMS polymers and ethylene dialkoxyalkylsilyl endblocked PDMS polymers, where preferred alkoxy groups include methoxy or ethoxy and a preferred alkyl group is methyl. Hydroxyl endblocked PDMS polymer is the more pre-

ferred diorganosiloxane polymer.

Component (B) is water. Our silicone emulsion is in the form of an oil-in-water emulsion where the diorganosiloxane polymers comprise a dispersed phase and water comprises a continuous phase. The water is usually present in the amount of 8 to 1000 parts by weight, based on 100 parts of the diorganosiloxane polymers. Preferably, water is present in 15 to 50 parts by weight, based on 100 parts of the same polymer. The water is added in one amount or the amounts can be added at varying points of the compounding process as desired. For example, in a preferred method using direct emulsification, a small amount of water, for example 2 to 5 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, is used to emulsify the diorganosiloxane and other components, as desired, and then the resulting emulsion is diluted with additional water to the desired polymer solids content.

Component (C) is a surfactant. The term "surfactant" describes a surface active agent selected from cationic surfactants, anionic surfactants, amphoteric surfactants, nonionic surfactants and mixtures thereof, which stabilize the dispersed phase of the emulsion. Each of these surfactants are known in the art as useful in stabilizing emulsions of diorganosiloxane polymers, whether individually or combined with another type of surfactant.

Suitable cationic surfactants are aliphatic fatty amines and their derivatives such as dodecylamine acetate, octadecylamine acetate and acetates of the amines of tallow fatty acids; homologues of aromatic amines having fatty chains such as dodecylanalin; fatty amides derived from aliphatic diamines such as undecylimidazoline; fatty amides derived from disubstituted amines such as oleylaminodiethylamine; derivatives of ethylene diamine; quaternary ammonium compounds such as tallow trimethyl ammonium chloride, dioctadecyl-dimethyl ammonium chloride, didodecylmethyl ammonium chloride and dihexadecyldimethyl ammonium chloride; amide derivatives of amino alcohols such as beta-hydroxyethyl-steraryl amide; amine salts of long chain fatty acids; quaternary ammonium bases derived from fatty amides of di-substituted diamines such as oleylbenzylamino-ethylene diethylamine hydrochloride; quaternary ammonium bases of the benzimidazolines such as methylheptadecyl benzimidazole hydrobromide; basic compounds of pyridinium and its derivatives such as cetylpyridinium chloride; sulfonium compounds such as octadecylsulfonium methyl sulfate; quaternary ammonium compounds of betaine such as betaine compounds of diethylamino acetic acid and octadecylchloromethyl ether; urethanes of ethylene diamine such as the condensation products of stearic acid and diethylene triamine; polyethylene diamines; and polypropanolpolyethanol amines.

Suitable anionic surfactants include sulfonic acids and their salt derivatives as described in US-A 3,294,725. These anionic surfactants are alkali metal sulfonates; sulfonated glycerol esters of fatty acids such as sulfonated monoglycerides of coconut oil acids; salts of sulfonated monovalent alcohol esters such as sodium oleylisethionate; amides of amino sulfonic acids such as the sodium salt of oleyl methyl tauride; sulfonated products of fatty acids nitriles such as palmitonitrile sulfonate; sulfonated aromatic hydrocarbons such as sodium alpha-naphthalene monosulfonate and dibutylododecylbenzenesulfonate (DBSA); condensation products of naphthalene sulfonic acids with formaldehyde; sodium octahydroanthrazene sulfonate; alkali metal alkyl sulfates, such as sodium lauryl sulfate; ether sulfates having alkyl groups of 8 or more carbon atoms; alkylarylsulfonates having 1 or more alkyl groups of 8 or more carbon atoms; and dialkylsulfonates, each alkyl group having 8 or more carbon atoms, such as dioctyl sulfosuccinate.

Suitable amphoteric surfactants are lecithin, glycinate, betaines, sultaines and alkyl aminopropionates. They are exemplified by coco-amphglycinate, coco-amphocarboxy-glycinates, coco-amidopropylbetaine, lauryl betaine, coco-amidopropylhydroxysultaine, laurylsultaine and coco-amphodipropionate.

Useful nonionic surfactants are polyoxyalkylene alkyl ethers, polyoxyalkylene sorbitan esters, polyoxyalkylene esters, polyoxyalkylene alkylphenyl ethers, ethoxylated amides, ethoxylated siloxanes, block copolymers of propylene oxide or ethylene oxide and others.

Anionic surfactants and nonionic surfactants are preferred. Nonionic surfactants such as polyoxyalkylene alkyl ethers, including Tergitol® TMN-6, Tergitol® TMN-10 and Triton® X-100 and mixtures of anionic surfactants such as dioctyl sulfosuccinates and nonionic surfactants are more preferred.

Generally, the amount of surfactants used is that amount which stabilizes the dispersed phase of the silicone emulsion. An amount from 0.1 to 10 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, is sufficient. Preferably, the surfactant amount is from 0.5 to 5 parts by weight, based on 100 parts by weight diorganosiloxane polymer. More preferably, the surfactant is an amount from 1.5 to 5 parts by weight, based on 100 parts of diorganosiloxane polymer.

Component (D) is a crosslinker. This ingredient is optional depending on the diorganosiloxane polymer. When the diorganosiloxane polymer has an average of more than 1.3 condensable or hydrolyzable groups per molecule, crosslinker is not necessary to crosslink the diorganosiloxane polymer. The condensable or hydrolyzable groups on different diorganosiloxane polymer molecules react with each other to form the crosslinked rubber particles which dry to form a silicone elastomer upon removal of water from said emulsion. Even though a crosslinker is not required, it may be desirable to use one.

When the diorganosiloxane polymer does not on average have more than 1.3 hydrolyzable or condensable groups, a crosslinker must be added to form the rubber particles which dry to a silicone elastomer upon water removal from the silicone emulsion.

Typically, the crosslinker is an organo silicon compound or a resin which contains on average per molecule, more

than 2 hydrolyzable groups or hydroxyl groups bonded to a silicon atom. The hydrolyzable groups useful for the crosslinker are the same as those described for substituent X of the diorganosiloxane polymer.

As long as the crosslinker contains on average more than 2 hydrolyzable groups or hydroxyl groups bonded to silicon and preferably at least 3 of these groups bonded to silicon, and depending on the groups bonded to the diorganosiloxane polymers, other types of groups may also be bonded to silicon. The molecular structure of the crosslinker is a silane or siloxane structure. In addition, the siloxane type crosslinkers may be straight chain, branched chain or cyclics. Examples of the groups, other than hydrolyzable groups, which are attached to silicon atoms of the crosslinkers, include hydrogen atom and the monovalent substituted or unsubstituted hydrocarbon groups described for R.

In essence, any known crosslinker, for crosslinking aqueous silicone emulsions in the presence of a tin condensation catalyst, can be used in our invention such as colloidal silica, alkali silicates, alkali siliconates, alkoxysilanes, alkenoxysilanes, oximosilanes, silazanes, aminoxysilanes, silicone resins and silicone hydrides. Examples of specific crosslinkers are low molecular weight organosilicon hydrides, such as polymethylhydrogensiloxane; low molecular weight copolymers containing methylhydrogensiloxy and dimethylsiloxy groups;  $-(OSi(OEt)_2)_n$ , ethylpolysilicate;  $(OSiMeC_2H_4Si(OMe)_3)_4$ ;  $(OSi-ON=CR'_2)_4$ ; methyltrimethoxysilane; methyltripropenoxysilane; tetraethylorthosilicate; isobutyltrimethoxysilane; ethyltriacetoxysilane; methyltriacetoxysilane; vinyltriacetoxysilane; vinyltrioximosilane and  $Me_3SiO(Me_2SiO)_3(Me(ON(Et)_2SiO)_5-SiMe_3$ , in each case where Me is methyl and Et is ethyl.

Preferred crosslinkers are silanes having at least three alkoxy groups. More preferred is when each alkoxy group has up to 8 carbon atoms. Most preferred is when each alkoxy group has up to 3 carbon atoms such as methyltrimethoxysilane, isobutyltrimethoxysilane, methyltriethoxysilane, methyltripropenoxysilane and chloropropyltrimethoxysilane.

Normally, the crosslinker, when used herein, is added in amount from 0.1 to 50 parts by weight, based on 100 parts by weight of diorganosiloxane polymer. Preferably, 1 to 10 parts by weight of diorganosiloxane polymer is added, with 2 to 5 parts by weight, per 100 parts of diorganosiloxane polymer being more preferred.

The crosslinker is added as a single species or as a mixture of two or more different species. The crosslinkers may be added before or after emulsification. For ease of compounding, however, it is preferred to add the crosslinker before emulsification.

Component (E) is a tin condensation catalyst that serves to accelerate the crosslinking reaction between diorganosiloxane polymers if they contain sufficient hydrolyzable groups or more typically between a diorganosiloxane polymer and a crosslinker. The catalyst is an organotin compound having a valency of +4 such as stannic tin (IV) compounds or a mixture of a tin (IV) and an organotin compound having a valency of +2, such as stannous tin (II) compounds. Stannic tin (IV) compounds are preferred. Examples of stannous tin compounds are organic stannous carboxylates such as stannous oleate, stannous octoate and stannous neodecanoate. Examples of stannic tin compounds include tin stannoxanes such as  $((C_4H_7)_2SnCl)_2O$  and  $(C_4H_7)_2-Sn(Cl)-OSn(OH)(C_4H_7)_2$  or stannic carboxylates having the formula  $R'_2Sn(OCOR'')_2$ , where each R' is individually selected from monovalent alkyl radicals having from 1 to 18 carbon atoms and R'' is individually selected from R' or  $-CH_2COR'$ , where R' is defined above. The tin catalyst can also be the reaction product of  $R'_2SnO$  with (a)  $R'_2Sn(OCOR')_2$ ; (b)  $R'_2Sn(OCOR')_2$  and a dicarboxylic acid anhydride; (c) a carboxylic acid; (d) secondary amines or N-acylated amino acids; (e)  $R'_sSn(SR')_{4-s}$ , where s is 1, 2 or 3; and (f) a carboxylic acid, an alcohol or an alcohol amine. The tin (IV) compound can also have the formulae  $R'_2DSn(OSnR'_2)_c-D$  or  $R'_2SnD_2$ , where R' is as defined above, D is a dicarboxylic acid monoester and c is a positive integer from 1 to 10;  $M-SnR'_2-(OSnR'_2)_x-M$ , where M is an alkoxy group or other radical capable of forming coordinative bonds with tin and x is a positive integer from 1 to 10; or  $R'_2Sn(OSiR'_3)_2$ .

Substituent R' is a monovalent alkyl group having from 1 to 18 carbon atoms. Examples of R' include methyl, ethyl, propyl, hexyl, dodecyl and octadecyl.

Substituent D is a dicarboxylic acid monoester such as ethyloxolate.

Substituent M is an alkoxy group or other radical capable of coordinating with tin, such as acetylacetonate.

The stannic carboxylates are the more preferred tin condensation catalysts, with dibutyltindiacetate being the most preferred.

It may be desirable to reduce the amount of the tin (IV) catalyst in our silicone emulsion. This is achieved by using known co-catalysts such as carboxylic acids or amines and salts of carboxylic acids or amines as described by Chu, H.K.; Cross, R.P.; and Crossan, D.I.; *J. Organomet. Chem.*, 1992, 425, 9-17.

Generally, the tin condensation catalyst is added in an amount from 0.01 to 5 parts by weight based on 100 parts by weight of diorganosiloxane polymer. Preferably, the catalyst is added from 0.05 to 2 parts by weight, per 100 parts of diorganosiloxane polymer; with 0.06 to 0.5 part by weight, based on 100 parts by weight of diorganosiloxane polymer, being more preferred.

The tin condensation catalyst is added as a single species or as a mixture of two or more different species. The tin condensation catalyst may also be added before or after emulsification. For ease of compounding, however, it is preferred to add the tin condensation catalyst prior to emulsification.

Component (F) is an aminofunctional siloxane that is formed by reacting components comprising an aminofunctional silane (II), having the formula  $A_3Si(CH_2)_p-(Z-(CH_2)_q)_rNR^3$ , with a hydroxy-endblocked organosiloxane (III) having the formula  $HO-(SiR^4)_b-OH$ . Both the aminofunctional silanes and the hydroxy-endblocked organosiloxanes are com-

mercially available or are prepared by known methods.

Substituent A is a hydrolyzable group. Hydrolyzable groups include any group attached to silicon that is hydrolyzed by water at room temperature. Suitable hydrolyzable groups represented by A are those hydrolyzable groups described for X.

Substituent A is preferably an alkoxy group and more preferably an alkoxy group having up to 8 carbon atoms. Illustrative examples of alkoxy groups are methoxy, ethoxy, propoxy, isobutoxy, pentoxy, hexoxy and 2-ethylhexoxy. It is most preferred for A to be an alkoxy group having up to 3 carbon atoms.

Substituent Z is an oxygen atom or  $\text{NR}^2$ , where  $\text{R}^2$  is individually selected from hydrogen atom or substituted and unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms. Substituent Z is preferably  $\text{NR}^2$ . Examples of the substituted and unsubstituted monovalent hydrocarbon radicals of  $\text{R}^2$  are the same as for substituent R. Preferably,  $\text{R}^2$  is hydrogen.

Subscript p is a positive integer from 2 to 10, preferably from 2 to 6, and most preferably 3.

Subscript q is a positive integer from 2 to 10, preferably from 2 to 6, and most preferably 2.

Subscript r is a positive integer from 0 to 3, preferably from 0 to 2, and most preferably 0 or 1.

Substituent  $\text{R}^3$  is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1 to 15 carbon atoms. Examples of these substituted and unsubstituted monovalent hydrocarbon radicals are the same as provided above for substituent R. In addition, substituent  $\text{R}^3$  can be a hydrogen atom.  $\text{R}^3$  is preferably a hydrogen atom.

Examples of aminofunctional silanes include

$(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_2-\text{NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_6-\text{NH}_2$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_4-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$  and  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2-\text{N}(\text{CH}_3)_2$ .

Preferred aminofunctional silanes are those containing primary amino groups, with  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$ ,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$ ,  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$  and  $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_6-\text{NH}_2$  being more preferred.

The aminofunctional silane is mixed with a hydroxy-endblocked organosiloxane (III) having the formula  $\text{HO}-(\text{SiR}^4)_b-\text{OH}$  to form the aminofunctional siloxane.

$\text{R}^4$  is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms. Examples of these substituted and unsubstituted monovalent hydrocarbon radicals are the same as for substituent R. Preferably, each  $\text{R}^4$  is methyl.

Subscript b represents the degree of polymerization in the hydroxy-endblocked organosiloxane and is from 4 to 80. Preferably b is 4 to 50, and more preferably, b is 6 to 20.

Short chain hydroxy endblocked organosiloxanes are preferred over those having a longer chain because an effective concentration of amino functionality can be obtained at a lower addition level of the aminofunctional siloxane when short chains are used. The optimum chain length and nature of the hydroxy endblocked organosiloxane is further determined by other parameters. One key parameter is the compatibility of the aminofunctional siloxane with the diorganosiloxane polymer and other components of the emulsion. Compatibility improves with increasing chain length of the hydroxy-endblocked organosiloxane and with chemical similarity of the various R substituents. For instance if the diorganosiloxane is substantially a PDMS polymer, it may be desirable to use a short chain PDMS for improved compatibility. Compatibility is important because it controls the partitioning of the aminofunctional siloxane between the water phase and the dispersed phase containing the diorganosiloxane polymer.

In a preferred embodiment, the aminofunctional siloxane is formed by reacting components comprising an aminofunctional silane (II), a hydroxy-endblocked organosiloxane (III) and a silane (IV) having the formula  $\text{R}^5_c\text{SiG}_{4-c}$ . This silane is commercially available or is prepared by known methods.

Substituent  $\text{R}^5$  is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms. Examples of these radicals are the same as provided above for substituent R. The preferred  $\text{R}^5$  radical is methyl.

Substituent G is a hydrolyzable group. Hydrolyzable groups useful for the invention are the same as described for X. Substituent G is preferably an alkoxy group and, more preferably, a methoxy or an ethoxy group.

Subscript c is 0, 1 or 2. Preferably, c is 0 or 1 and, more preferably, c is 1.

Examples of silane (IV) are the same as examples provided above for the crosslinker as well as dimethyldimethoxysilane, dimethyldiethoxysilane, ethylmethyldimethoxysilane and diisobutyldimethoxysilane. Preferably the silane is an alkoxysilane, with methyltrimethoxysilane and methyltriethoxysilane being more preferable, and with methyltrimethoxysilane being most preferred.

It is also preferable for the hydrolyzable group on the silane to be of the same chemical nature as the hydrolyzable group on the crosslinker. Thus, if the hydrolyzable groups on the crosslinker are methoxy groups, then it is preferable for the hydrolyzable groups on the silane to be alkoxy groups, although they do not necessarily need to be methoxy groups. Combinations of leaving groups which may give risk to incompatibility or exothermic acid/base reactions should be avoided.

The addition of component (IV) to components (II) and (III) provides improved shelf life for the aminofunctional

siloxane. Mixing of components (II) and (III), at a molar ratio of (II) to (III) of less than 1 and without addition of component (IV), results in increased viscosity and gelling of the aminofunctional siloxane within 2 to 28 days, the actual time period depending on the amount of aminofunctional silane added.

Components (II), (III) and (IV) are mixed in varying molar ratios to form the aminofunctional siloxane. Normally, the components are mixed such that the molar ratio of components (II) and (IV) to component (III) is at least 1:1, preferably at least 1.1:1 and the molar ratio of component (IV) to component (II) is between 0 and 2 inclusive. The most preferred molar ratio of component (II) to component (III) is from 0.2 to 0.8 and the most preferred molar ratio of component (IV) to component (III) is from 0.2 to 0.8.

The aminofunctional siloxane is formed by mixing components comprising an aminofunctional silane (II) and a hydroxy-endblocked organosiloxane (III), or in a preferred embodiment by mixing components comprising an aminofunctional silane (II), a hydroxy-endblocked organosiloxane and a silane (IV), and in each case allowing them to react. These components are added as a single species or as a mixture of two or more different species. The mixing is done by blending the components together at room temperature or other conventional methods for mixing compounds. The order of mixing is not critical although it is preferred to mix component (III) into component (II) and to then mix in component (IV). Components (II), (III) and (IV) can be mixed neat, in solution or in solvent, although it is preferred to add them neat.

The aminofunctional siloxane is added to the other ingredients of the silicone emulsion until the reaction between the components is substantially complete. The amount of time necessary for this depends on the specific compounds used and can be determined experimentally. Typical reaction times range from 5 to 24 hours. If desired, the mixture can be heated in the range of 50°C. to 70°C. which will reduce the reaction time to less than 2 hours.

An effective amount of aminofunctional siloxane is that amount which is added to produce improved adhesion to substrates by a silicone elastomer formed from the silicone emulsion upon removal of water. The amount of aminofunctional siloxane required depends on the molecular weight of the hydroxy-endblocked organosiloxane. Typically, adding the aminofunctional siloxane in an amount from 0.10 to 10 parts by weight, based on 100 parts by weight of diorganosiloxane polymer will achieve a required minimum concentration of 0.0005 parts by weight of aminofunctionality, preferably 0.005 parts by weight of aminofunctionality, in each case based on 100 parts by weight diorganosiloxane polymer. As used herein, "parts by weight of aminofunctionality" means the weight percent of primary and secondary amino groups in the aminofunctional siloxane, multiplied by the parts by weight of aminofunctional siloxane in the formulation, based on 100 parts by weight of diorganosiloxane polymer.

The aminofunctional siloxane is added before or after emulsification. If the aminofunctional siloxane is added after emulsification, it is preferred that the aminofunctional siloxane be added within 8 hours of the emulsification, and more preferably within 2 to 5 hours to ensure that the adhesive properties of the silicone elastomer obtained upon removal of water are not reduced. For ease of compounding, it is preferred to add the aminofunctional siloxane prior to emulsification.

Component (G) is an acid and it is used as an optional ingredient. It is believed that acid assists in the incorporation of the aminofunctional siloxane into the emulsion. The acid may be added as a separate ingredient or as part of another component. For example, if dibutyltin diacetate (DBTDA) is used as the tin condensation catalyst, the DBTDA either already contains acetic acid if used in solution or will form acetic acid upon addition to the aqueous emulsion. Any acid may be used in this invention, such as HCl and H<sub>2</sub>SO<sub>4</sub>, or organic acids such as carboxylic acids. Carboxylic acids are preferred because carboxylic acids and their corresponding amine salts also act as a condensation co-catalyst with the tin condensation catalyst. Examples of carboxylic acids are acetic, formic, propionic and crotonic acids. Acetic acid is the most preferred acid. Since carboxylic acids and their corresponding amine salts will act as a co-catalyst, when a carboxylic acid is added, the amount of tin condensation catalyst added typically may be reduced.

Usually, the acid is added in an amount from 0.05 to 0.3 part by weight, based on 100 parts by weight of diorganosiloxane polymer. Preferably, the acid is added in an amount from 0.06 to 0.2 parts by weight, with 0.07 to 0.13 part by weight, based on 100 parts by weight of diorganosiloxane polymer being more preferred.

The acid is added as a single species or as a mixture of two or more species. The acid may be added before or after emulsification. It is preferred to add the acid prior to crosslinking of the diorganosiloxane polymers, therefore before the addition of the tin condensation catalyst and any required crosslinker.

Additional optional ingredients such as fillers and other ingredients may be added with the other components, as desired, to affect certain performance properties of the silicone emulsion or the silicone elastomer formed therefrom. Reinforcing and extending fillers include calcium carbonate, titanium dioxide, zinc oxide, iron oxide or kaolin clay. Fillers which may be used to achieve fire retardancy or electrical arc resistance include aluminum trihydrate, fumed titania or zinc borate. Other optional ingredients, including pigments, stabilizers and in-situ reinforcement resins may also be added to the silicone emulsion.

All of these additional optional ingredients should be tested to ensure that they do not adversely affect the adhesive properties and the shelf life of the silicone emulsion or the silicone elastomer formed upon drying the emulsion. The characteristics of the aqueous silicone emulsion and the silicone elastomer can be varied to give the desired characteristics by varying these additional optional ingredients.

The particle size of the silicone emulsion does not limit the present invention as the improved adhesion to substrates occurs without regard to particle size. However, particle size should be such that the silicone emulsion remains stable for a useful length of time, which is usually on the order of several months to several years. Particle sizes of 200 to 100 nm typically provide this degree of emulsion stability.

The silicone emulsions of this invention may be formed by different methods. For example, the silicone emulsions can be prepared by the process of emulsion polymerization, as taught in US-As 2,891,920; 3,294,725; 3,355,406; 3,360,491 and 3,697,469.

With emulsion polymerization, cyclic or linear siloxane oligomers are dispersed in water with a surfactant to form a premixture. Typically, amphoteric, anionic or cationic surfactants are used or mixtures of amphoteric, cationic or anionic surfactants with nonionic surfactants will also work. The premixture is then mixed at high shear until an emulsion comprising an aqueous phase and a dispersed phase comprising droplets of siloxane oligomers, having particle sizes of between 100-5000 nm, is formed. The mixing can take place in any type of commercial mixing equipment, said mixers being well known to those skilled in the art. To adjust pH, an acid or base may be added to the emulsion or it is added to the premixture. Alternatively, the surfactant may be converted to its acidic or basic form using an ion exchange procedure as taught in US-A 3,697,469. Although the polymerization will proceed satisfactorily at room temperature, it can be run at elevated temperatures as well, a preferred temperature range being 25°C. to 80°C. The time of polymerization will generally take from 1 to 24 hours depending on the temperature and the desired molecular weight of the polymer. After the diorganosiloxane polymer has reached the desired molecular weight, polymerization is terminated by neutralizing the emulsion.

A crosslinker, if necessary or desired, and a tin condensation catalyst can be added prior to emulsification or after polymerization. Oftentimes, however, the crosslinker and tin condensation catalyst will be added to the emulsion after polymerization is complete. The crosslinker, in this situation, must be capable of migrating from the water into the dispersed phase and still maintain its reactivity.

The aminofunctional siloxane is added at any time during emulsion polymerization, for example as part of the premixture prior to emulsification or after the premixture is emulsified, either prior to or after polymerization. If the aminofunctional siloxane is added after emulsification, it is preferred to add it within 8 hours.

Additional amounts of water may be also be added at any stage of compounding if a lower polymer solids content is desired. Typical polymer solids content are 20-75%. Preferred polymer solids contents are 40-75%.

The acid may be added after polymerization is complete, separately or as part of another component, i.e. for example, DBDTA will form acetic acid upon addition to water.

Any other optional ingredients, such as fillers, pigments, stabilizers, in-situ reinforcement resins, etc. may also be added at any time after the polymerization is complete.

A preferred method for preparing the aqueous silicone emulsions is by a direct emulsification method which is well known to those skilled in the art and taught in US-A 4,177,177 or EP-A 0 739 947; 0 739 928 and 0 739 929.

With direct emulsification, a mixture of preformed diorganosiloxane polymers, surfactant and water is emulsified at a temperature of 10°C. to 70°C. by mixing with sufficient shear for a sufficient period of time. The diorganosiloxane polymers useful in this process are characterized as having a viscosity of 5000 to 500,000 mPa · s at 25°C. However, higher molecular weight polymers can be used if the viscosity is adjusted using solvent, polymer blending and so forth.

Typically, amphoteric, anionic, cationic or non-ionic surfactants are used singly or as mixtures. The mixing takes place in any type of commercial mixing equipment, said mixers being well known to those skilled in the art.

A crosslinker, if necessary or desired, and a tin condensation catalyst can be added prior to emulsification or after emulsification. Oftentimes, however, the crosslinker and tin condensation catalyst will be added before emulsification. If added after emulsification, the crosslinker must be capable of migrating from the water into the dispersed phase and still maintain its reactivity.

The aminofunctional siloxane may be added at any time, before or after the emulsification. If the aminofunctional siloxane is added after emulsification, it is preferred to add it within 8 hours of crosslinking the emulsion.

Additional amounts of water may be also be added at any stage of compounding if a lower polymer solids content is desired. Typical polymer solids content are 10-96%. Preferred polymer solids contents are 20-85%, with 40-85% being more preferred.

The acid may also be added at any time, separately or as part of another component, i.e., for example, DBDTA will form acetic acid upon addition to water. In a preferred method, a carboxylic acid and the aminofunctional siloxane are added before crosslinking. This enables the amount of tin condensation catalyst to be reduced if desired.

Any optional ingredients, such as fillers, pigments, stabilizers, in-situ reinforcement resins etc. may also be added at any stage of compounding.

In a more preferred method, the aqueous silicone emulsion is formed by mixing at high shear 100 parts by weight of a diorganosiloxane polymer, wherein X is a hydroxy group, n is 2, Y is Si and R and R<sup>1</sup> are each a methyl radical; 3 parts of water; 2 parts of a polyoxyalkylene alkyl ether surfactant; 0.06 part by weight of dibutyltin diacetate catalyst; 1 part by weight of the aminofunctional siloxane that is formed by reacting components comprising the aminofunctional silane (II) (CH<sub>3</sub>O)<sub>3</sub>Si-(CH<sub>2</sub>)<sub>3</sub>-NH-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>2</sub>, the hydroxy-endblocked organosiloxane (III) HO-(Si(CH<sub>3</sub>)<sub>2</sub>)<sub>b</sub>-OH, where



b is 7 to 9 and the silane (IV) methyltrimethoxysilane, provided there is 0.005 part by weight of aminofunctionality, and provided further, the molar ratio of component (II) and component (IV) to component (III) is at least 1 and the molar ratio of component (IV) to component (II) is no greater than 2; and 0.1 part acetic acid to form a high solids emulsion, diluting the high solids emulsion with water as desired and then crosslinking the emulsion by adding 0.8 part by weight of isobutyltrimethoxysilane crosslinker.

The silicone elastomer formed from our silicone emulsion upon removal of water has improved adhesion to substrates. In addition, our silicone emulsion has a longer shelf life relative to prior art emulsions.

The following examples are presented to further illustrate the compositions of this invention. In the following examples, if not otherwise noted, the wet emulsions were cast into films 1 day after the emulsions were made, and the films were allowed to dry for 7 days prior to testing.

Durometer results were obtained by the method described in ASTM C661 "Indentation Hardness of Elastomeric-Type Sealants by Means of a Durometer". Tensile and elongation results were obtained by the method described in ASTM D412 "Vulcanized Rubber and Thermoplastic Rubbers and Thermoplastic Elastomers - Tension" using dumbbell specimens with an L dimension equal to 1.27 mm. Shore A hardness values were obtained by the method described in ASTM C-661 "Indentation Hardness of Elastomeric Type Sealants by Means of a Durometer."

As used herein, "Me" means methyl, "Et" means ethyl and "laboratory conditions" means a temperature of 23°C.  $\pm$  2°C. and 50%  $\pm$  5% relative humidity.

#### (A) Method for Evaluation of Adhesion

Samples were tooled as 50 mm long and 18 mm wide beads on various substrates. The adhesion was evaluated by under-cutting the bead at the sealant/substrate interface with a razor blade and by pulling the bead manually at an angle of 45° against the horizontal substrate surface. The adhesion was rated "excellent", if the bead failed cohesively. The adhesion was rated "good", if the bead failed adhesively and it took considerable force to remove the bead from the substrate surface. The adhesion was rated "poor", if the bead failed adhesively at a relatively low peel force.

#### Example 1

5000 parts of a hydroxy-endblocked polydimethylsiloxane (PDMS) polymer having a viscosity of 50 Pa  $\cdot$  s at 25°C., 100 parts of Tergitol® TMN-6, a nonionic surfactant of ethoxylated trimethylnonanol and 100 parts of deionized (DI) water were charged to a 10 liter Turello™ mixer.

The mixture was stirred under vacuum for 5 minutes with the disperser blades rotating at 1,200 rpm. After mixing, inspection showed a clear, non flowing (thixotropic) gel indicating the formation of a high solids, oil-in-water emulsion. Agitation was begun again with the disperser blades rotating at 600 rpm and 250 parts of DI water were added. Vacuum was applied and the emulsion was agitated for another two minutes with the disperser blades rotating at 1,200 rpm. Another inspection found a now milky white emulsion. Agitation was started again with the disperser blades rotating at 600 rpm and 1000 parts of DI water were added in 2 equal increments. Vacuum was applied, and the mixture stirred for 2 minutes between additions. A milky white, smooth oil-in-water emulsion was formed, which was free of lumps and gels. To this emulsion, 50 parts of an aminofunctional siloxane (AFF2) which had been obtained by cold blending 74.6 parts of a hydroxy-endblocked PDMS fluid with a degree of polymerization (DP) of 7 to 9 and a viscosity of 0.04 Pa  $\cdot$  s at 25°C. with 15.2 parts of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS) and 10.2 parts methyltrimethoxysilane (MTM), were added. Agitation of the mixture was started with the disperser blades rotating at 600 rpm, vacuum applied and the mixture was stirred for 2 minutes. 40 parts of IBTMS (isobutyltrimethoxysilane) were then added and mixture was stirred for another 2 minutes under vacuum. Next, 10 parts of DBTDA (dibutyltin diacetate) were added and the mixture was stirred for 2 minutes under vacuum with the disperser blades rotating at 600 rpm. The crosslinked silicone emulsion was packaged into Semco® cartridges which were centrifuged to remove any trapped air.

After aging the above crosslinked silicone emulsion for 18 hours at room temperature, a sample was cooled into a 2.54 mm [100 mil.] thick film and allowed to cure under laboratory conditions for 7 days. The cured, translucent silicone elastomer had a tensile strength of 0.5 MPa (80 psi), a maximum elongation of 2000%, and a Shore A durometer of 10. Further samples of this aged silicone emulsion were tooled as 50 mm long and 18 mm wide beads onto 16 different substrates and allowed to cure under laboratory conditions for 7 days. One commercially available, calcium carbonate filled silicone latex sealant (Dow Corning® Silicone Plus) and one commercially available, moisture curable RTV alkoxy cure silicone sealant (General Electric® GE II) (non-latex) were evaluated under identical conditions for comparative purposes. Table I summarizes the adhesion results.

Table 1

| Sealant Adhesion                  |           |               |           |
|-----------------------------------|-----------|---------------|-----------|
| Substrate                         | Example 1 | Silicone Plus | GE II     |
| Ceramic Tile                      | excellent | poor          | excellent |
| Duracore                          | poor      | good          | good      |
| Concrete                          | excellent | good          | good      |
| Corian                            | poor      | good          | excellent |
| Painted Pine (Alkyd Paint)        | excellent | excellent     | excellent |
| Painted Pine (Latex Paint)        | excellent | excellent     | excellent |
| Red Wood                          | excellent | excellent     | excellent |
| Anodized Aluminum                 | excellent | excellent     | excellent |
| Polyvinylchloride (unplasticized) | excellent | good          | excellent |
| Glass                             | excellent | good          | excellent |
| Brass                             | excellent | excellent     | excellent |
| Pine                              | excellent | excellent     | excellent |
| Polycarbonate                     | poor      | good          | poor      |
| Stainless Steel                   | excellent | excellent     | good      |
| Mortar                            | excellent | good          | good      |
| PMMA (Polymethylmethacrylate)     | poor      | good          | poor      |

Example 2

(a) 100 parts of a hydroxy-terminated PDMS polymer having a viscosity of 50 Pa · s at 25°C., and 1 part of the aminofunctional siloxane prepared in Example 1 (AFF2), were charged to a 350 ml Whip Mix™ pot and stirred for 30 seconds under vacuum. 0.06 part of DBTDA was then added and the mixture was stirred for another 30 seconds under vacuum. 0.1 part of glacial acetic acid was added and the mixture was stirred for another 30 seconds under vacuum. Next, 2 parts of Tergitol® TMN-6, a nonionic surfactant ethoxylated trimethylnonanol and 3 parts of DI water were added and the mixture stirred for another 30 seconds under vacuum, yielding a slightly translucent, nonflowable, high solids oil-in-water emulsion. DI water was then added in 4 increments of 4 parts each with 30 seconds of stirring under vacuum between additions. 0.8 parts of IBTMS was added and the mixture stirred for another 30 seconds under vacuum. The silicone emulsion was packaged into a Semco® cartridge and centrifuged to remove any trapped air. After aging for 18 hours at room temperature, a sample was tooled into a 2.54 mm [100 mils] thick film and allowed to cure under laboratory conditions for 7 days. The cured, translucent silicone latex elastomer had a tensile strength of 0.25 MPa (40 psi), a maximum elongation of 1570%, and a Shore A durometer of 6. Further samples of the 18 hr aged silicone emulsion were tooled as 50 mm long and 18 mm wide beads onto glass, concrete, painted pine and red wood as substrates and allowed to cure under laboratory conditions for 14 days. Adhesion of the silicone latex was evaluated as described in (A) above. The latex exhibited excellent adhesion (cohesive failure mode) to all of the substrates. Further samples of the silicone emulsion were tested for adhesion as described in (A) above after shelf-aging the wet silicone emulsion under laboratory conditions for 4 weeks. The latex exhibited excellent adhesion (cohesive failure mode) to all the substrates.

(b) The same procedure was followed as in Example 2(a) except no aminofunctional siloxane was added. The cured, translucent silicone elastomer had a tensile strength of 0.6 MPa (86 psi), a maximum elongation of 1080%, and a Shore A durometer of 11. The elastomer exhibited poor adhesion on glass and good adhesion concrete, painted pine and red wood. Further samples of that emulsion were tested for adhesion as described in (A) after shelf-aging the wet silicone emulsion under laboratory conditions for 4 weeks. The sealant exhibited poor adhesion on glass and good adhesion on concrete, painted pine and red wood.

(c) This example was prepared according to the procedure of Example 2(a) above except 0.152 part of 3-aminopropyltriethoxysilane (APTES) was substituted for the aminofunctional siloxane. The cured, translucent silicone elastomer had a tensile strength of 0.32 MPa (46 psi), a maximum elongation of 1280%, and a Shore A durometer of 6. The elastomer exhibited excellent adhesion (cohesive failure mode) to glass, concrete, painted pine and red wood. Further samples of the silicone emulsion were tested for adhesion as described in (A) after shelf-aging the wet silicone emulsion under laboratory conditions for 4 weeks. The sealant exhibited poor adhesion to glass and good adhesion to concrete, painted pine and red wood.

### Example 3

50 parts of a hydroxy-endblocked PDMS polymer having a viscosity of 50 Pa · s at 25°C., and 0.03 part of DBTDA were charged to a 100 ml mixer cup and stirred in a Hauschild™ mixer for 10 seconds. Then 0.5 part of the aminofunctional siloxane of Example 1 (AFF2) was added, and the mixture was stirred for another 10 seconds in the mixer. Then 0.375 part of IBTMS was added, and the mixture was stirred for another 10 seconds. Then 1 part Tergitol® TMN-6 surfactant and 1.5 parts of 0.072 molar aqueous solution of glacial acetic acid in DI water were added and the mixture was stirred for another 10 seconds to form a high solids, oil-in-water emulsion. This emulsion was further diluted by sequential addition of 3, 3 and 4 parts of 0.072 molar acetic acid, with the mixture being stirred for 10 seconds on the mixer between additions. The silicone emulsion was a milky white material which was transferred into a Semco® cartridge and centrifuged to remove any trapped air. After aging for 18 hr at room temperature, a sample was tooled into a 2.54 mm [100 mils] thick film and allowed to cure under laboratory conditions for 7 days. The cured, translucent silicone elastomer had a tensile strength of 0.34 MPa (50 psi), a maximum elongation of 1290%, and a Shore A durometer of 6. Further samples of the 18 hour aged silicone emulsion were tooled as 50 mm long and 18 mm wide beads onto glass, concrete, painted pine and red wood as substrates and allowed to cure under laboratory conditions for 14 days. The sealant exhibited excellent adhesion (cohesive failure mode) to all substrates tested.

### Example 4

Aminofunctional siloxanes having different siloxane chain lengths were prepared by cold blending distilled AEAPTMS, hydroxy-endblocked organosiloxanes (siloxane diols) and MTM in a polyethylene vessel. The mixture was allowed to react for 24 hours, after which time 100% of the hydroxy functionality of the hydroxy-endblocked siloxane had disappeared as determined by gas liquid chromatography (GLC). Table 2 shows the ratios, in parts by weight, at which the aminofunctional silane, the siloxane diols of various chain lengths, and the MTM were blended. Each siloxane diol consisted of a distribution of different chain length siloxane diols, their number average molecular weight corresponding to a DP of 4, 8 and 39. The mix ratios reported in Table 2 were then calculated assuming the above DPs and a molar ratio of siloxane diol to AEAPTMS to MTM of 0.122 to 0.068 to 0.075.

Table 2

| Components (in Parts) | Aminofunctional Siloxanes |      |      |
|-----------------------|---------------------------|------|------|
|                       | AFF1                      | AFF2 | AFF3 |
| Siloxane diol DP=4    | 60.2                      |      |      |
| Siloxane diol DP=8    |                           | 74.6 |      |
| Siloxane diol DP=39   |                           |      | 93.3 |
| distilled AEAPTMS     | 23.8                      | 15.2 | 4    |
| MTM                   | 16                        | 10.2 | 2.7  |

The aminofunctional siloxane (AFF2) is the aminofunctional siloxane used above in Examples 1, 2 and in any other example which includes AFF2.

Three elastomer formulations were prepared each using one of these aminofunctional siloxanes. The addition level of AFF1 and AFF3 were based on an equimolar aminofunctional silane level, based on 1 weight part of AFF2 as a reference. For each formulation, 100 parts of a hydroxy-endblocked PDMS polymer having a viscosity of 50 Pa · s at 25°C., and either 0.64 part AFF1, 1 part AFF2 or 3.8 parts AFF3 were charged to a 350 ml Whip Mix™ mixer and each mixture was stirred for 30 seconds under vacuum. To these mixtures 0.06 part DBTDA and 0.75 part IBTMS were added and the mixtures stirred for another 30 seconds under vacuum. 0.10 part of glacial acetic acid were added and the mixtures stirred for another 30 seconds under vacuum. Then 2 parts of Tergitol® TMN-6 surfactant and 3 parts of

DI water were added and the mixtures stirred for another 30 seconds each forming high solids, oil-in-water emulsions. These emulsions were further diluted by sequential addition of 5 increments of DI water of 4 parts each with 30 seconds of stirring under vacuum between additions. The silicone emulsions were transferred into Semco<sup>®</sup> cartridges and centrifuged to remove any trapped air. After aging for 18 hr at room temperature, a sample of each formulation was tooled into a 2.54 mm [100 mils] thick film and allowed to cure under laboratory conditions 7 days. See Table 2(b) for physical property data of the sealant formulations.

Table 2(b)

| Physical Properties | Sealant Formulations |        |        |
|---------------------|----------------------|--------|--------|
|                     | S-AFF1               | S-AFF2 | S-AFF3 |
| Tensile (MPa)       | 0.41                 | 0.28   | 0.35   |
| Max. Elongation (%) | 2570                 | 1480   | 730    |
| Shore A Durometer   | 2                    | 3      | 3      |

Further samples of the 18 hour aged silicone emulsions were tooled as 50 mm long and 18 mm wide beads onto glass and allowed to cure under laboratory conditions for 14 days. All samples exhibited excellent adhesion (cohesive failure mode) to the glass.

#### Example 5

Aminofunctional siloxanes were prepared by cold blending an aminofunctional silane bearing a primary, secondary or tertiary amino group, a siloxane diol with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C. and MTM in a polyethylene vessel. The mixture was allowed to react for 24 hr, after which time 100% of the -OH functionality of the siloxane diol had disappeared as determined by GLC. The following aminofunctional silanes were evaluated: (a) APTES, H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (primary amine) (b) AEAPTMS (primary and secondary amine groups), (c) bis(trimethoxysilylpropyl)amine (CH<sub>3</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub> (secondary amine) and (d) N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole, (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>-[N-CH=N-CH<sub>2</sub>-CH<sub>2</sub>]-, where the -N-CH=N-CH<sub>2</sub>-CH<sub>2</sub>- portion of the molecule is a cyclic radical endblocked siloxane and MTM were blended.

Table 3

| Components (in parts)                               | Aminofunctional Siloxanes |      |       |       |
|---|---------------------------|------|-------|-------|
|   | AFF2                      | AFF4 | AFF5  | AFF6  |
| Siloxane diol DP=8                                  | 74.6                      | 74.6 | 69.06 | 72.1  |
| (a)   |                           | 15.2 |       |       |
| (b)   | 15.2                      |      |       |       |
| (c)   |                           |      | 21.5  |       |
| (d)   |                           |      |       | 18.04 |
| MTM   | 10.2                      | 10.2 | 9.44  | 9.86  |
| * where (a), (b), (c) and (d) are as defined above. |                           |      |       |       |

Four formulations were prepared following the procedure of Example 4 above, except each formulation contained 1 part of one of the aminofunctional siloxanes AFF2, AFF4, AFF5 or AFF6. The silicone emulsions were then packaged and tested for adhesion as described in Example 4. Samples formulated with AFF2 or AFF4 showed cohesive failure mode to glass, while the samples formulated with AFF5 or AFF6 showed adhesive failure mode to glass.

**Example 6**

Aminofunctional siloxanes were prepared by cold blending AEAPTMS at half, twice or triple the molar levels used in AFF2 of Example 4. A hydroxy-endblocked PDMS organosiloxane with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C. (siloxane diol) was added with MTM in a polyethylene vessel. The mixture was allowed to react for 24 hours, after which time 100% of the -OH functionality of the siloxane diol had disappeared as determined by GLC. Table 4 shows the compositions of the aminofunctional siloxanes prepared.

Table 4

| Components (in parts) | Aminofunctional Siloxanes |                    |                  |                  |
|-----------------------|---------------------------|--------------------|------------------|------------------|
|                       | AFF2 (1 x molar)          | AFF7 (1/2 x molar) | AFF8 (2 x molar) | AFF9 (3 x molar) |
| Siloxane diol DP=8    | 74.6                      | 80.74              | 64.76            | 57.21            |
| AEAPTMS               | 15.2                      | 8.23               | 26.39            | 34.97            |
| MTM                   | 10.2                      | 11.03              | 8.85             | 7.82             |

Four formulations were prepared using one of the above aminofunctional siloxanes AFF2, AFF7, AFF8 and AFF9. The addition level of AFF2, AFF7, AFF8 or AFF9 to the silicone emulsion formulations was kept constant at 1 part based on 100 parts of PDMS polymer. These formulations were prepared, packaged and tested for adhesion as described in Example 4. Samples formulated with AFF2, AFF8 or AFF9 showed cohesive failure mode to glass, while the sample prepared with AFF7 showed adhesive failure mode to glass.

A further experiment was performed by mixing equal parts of AFF2 and AFF7 to form a 0.75x molar (AFF2/7) and adding 1 part of this blend based on 100 parts of PDMS polymer in a formulation. This elastomer when cured and tested as described above, showed cohesive failure mode to glass. This experiment indicated that the minimum amount of aminofunctionality required in the formulation to obtain cohesive failure mode to glass is  $\geq 5 \times 10^{-4}$  parts by weight based on 100 parts of PDMS polymer.

Physical properties were obtained on formulations that were allowed to rest for 18 hr prior to tooling samples into a 2.54 mm [100 mils] thick films, which then were cured under laboratory conditions for 14 days. Table 5 shows the properties of the various formulations.

Table 5

| Properties             | Sealant Formulations |          |          |          |          |
|------------------------|----------------------|----------|----------|----------|----------|
|                        | S-AFF2               | S-AFF7   | S-AFF8   | S-AFF9   | S-AFF2/7 |
| Adhesion to Glass      | cohesive             | adhesive | cohesive | cohesive | cohesive |
| Durometer              | 5                    | 8        | 2        | 0        | 6        |
| Tensile (MPa)          | 0.32                 | 0.36     | 0.17     | 0.12     | 0.34     |
| Maximum Elongation (%) | 1,280                | 1,480    | 1,840    | 2,480    | 1,290    |

As seen from Table 5, the increase of aminofunctional silane content in the aminofunctional siloxane leads to a decrease in durometer and tensile and an increase in the maximum elongation of the elastomer. Also, high levels of aminofunctional silane in the formulation (incorporated via the aminofunctional siloxane) leads to longer induction times (up to 10 days) before the elastomer will cure upon drying down. Thus, high levels of aminofunctional silane may not be desirable.

To determine the stability of the various aminofunctional fluids of Example 6, 15 g samples of each aminofunctional siloxane were placed in polyethylene bottles, purged with nitrogen and stored in a 50°C. oven. AFF7, having the lowest amount of aminofunctional silane gelled within 7 days storage. No gelation occurred for the remaining aminofunctional siloxanes over a 30 day storage period.

**Example 7**

Aminofunctional siloxanes were prepared by cold blending AEAPTMS, APMDSE or APTES, a siloxane diol with a

## EP 0 780 421 A2

DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C., and MTM in a polyethylene vessel. The mixture was allowed to react for 24 hr, after which time 100% of the -OH functionality of the siloxane diol had disappeared as determined by GLC. Table 6 shows the compositions of the aminofunctional siloxanes prepared.

Table 6

| Components (in Parts) | Aminofunctional Siloxanes |       |       |
|-----------------------|---------------------------|-------|-------|
|                       | AFF2                      | AFF10 | AFF11 |
| Siloxane diol DP=8    | 74.6                      | 76.2  | 74.67 |
| AEAPTMS               | 15.2                      | --    | --    |
| APMDES                | --                        | 13.38 | --    |
| APTES                 | --                        | --    | 15.12 |
| MTM                   | 10.2                      | 10.42 | 10.21 |

AFF2, AFF10 and AFF11 were each evaluated in elastomer formulations. In each case the addition level of AFF2, AFF10 or AFF11 was kept constant at 1 part based on 100 parts PDMS polymer. These formulations were prepared, packaged and tested for adhesion as described in Example 4. All samples formulated showed cohesive failure mode to glass.

To determine the stability of AFF2, AFF10 and AFF11 of this Example 7, 15 g samples of each aminofunctional siloxane were placed in polyethylene bottles, purged with nitrogen and stored in a 50°C. oven. AFF10, the aminofunctional siloxane prepared with APMDES gelled within 4 weeks of storage. No gellation occurred with AFF2 and AFF11 over the same storage period.

### Example 8

Aminofunctional siloxanes were prepared by cold blending AEAPTMS at the molar level used for AFF2 in Example 4, a siloxane diol with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C., and an alkoxysilane in a polyethylene vessel. The following alkoxysilanes were used: MTM, tetraethyl orthosilicate (TEOS) and n-propyl orthosilicate (NPOS). The mixtures were allowed to react for 24 hours after which time 100% of the -OH functionality of the siloxane diol had disappeared as determined by GLC. Table 7 shows the composition of each aminofunctional siloxane prepared.

Table 7

| Components (in parts) | Aminofunctional Siloxanes |       |       |
|-----------------------|---------------------------|-------|-------|
|                       | AFF2                      | AFF12 | AFF13 |
| Siloxane diol DP=8    | 74.6                      | 71.59 | 68.07 |
| AEAPTMS               | 15.2                      | 14.59 | 13.87 |
| MTM                   | 10.2                      | --    | --    |
| TEOS                  | --                        | 13.82 | --    |
| NPOS                  | --                        | --    | 18.06 |

AFF2, AFF12 and AFF13 were each evaluated in elastomer formulations. In each case the addition level of AFF2, AFF12 or AFF13 was kept constant at 1 part based on 100 parts PDMS polymer. The formulations were prepared, packaged and tested for adhesion as described in Example 4. All samples formulated showed cohesive failure mode to glass. The elastomers were also tested for freeze/thaw stability and were found to pass 10 ASTM freeze/thaw cycles.

### Example 9

An aminofunctional siloxane was prepared by cold blending AEAPTMS at the molar level used for AFF2 in Example 4, a siloxane diol with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C., and a mixture containing various alkoxyoxi-

mosilanes in a polyethylene vessel. The alkoxyoximosilane mixture contained 3% tetra(methylethylketoximo)silane (TOS), 84% of tri and dioximosilane, 10% mono oximosilane, where the other groups on the molecule are ethoxy groups and 2% methylethylketoxime solvent. The mixture was allowed to react for 24 hours, after which time 100% of the -OH functionality of the siloxane diol had disappeared as determined by GC. AFF2 was also prepared. Table 8 shows the composition of the aminofunctional siloxanes prepared.

Table 8

| Aminofunctional<br>Siloxane Components<br>(in parts) | Aminofunctional Siloxanes |       |
|--|---------------------------|-------|
|  | AFF2                      | AFF14 |
| Siloxane diol DP=8                                   | 74.6                      | 67.88 |
| AEAPTMS  | 15.2                      | 13.83 |
| MTM  | 10.2                      | --    |
| TOS  | --                        | 18.19 |

AFF2 and AFF14 were each evaluated in elastomer formulations. In each case the addition level of AFF2 or AFF14 was kept constant at 1 part based on 100 parts PDMS polymer. These formulations were prepared, packaged and tested as described in Example 4. All samples formulated showed cohesive failure mode to glass. They were also tested for freeze/thaw stability and were found to pass 10 ASTM freeze/thaw cycles.

#### Example 10

The following cold blends were prepared in a polyethylene vessel and allowed to react for 24 hours to evaluate the effects of binary mixture of the components comprising the aminofunctional siloxanes:

- (a) a siloxane diol with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C. blended with AEAPTMS;
- (b) a siloxane diol with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C. blended with MTM; and
- (c) MTM blended with AEAPTMS.

Table 9 shows the composition of the various functional fluids prepared.

Table 9

| Components (in parts) | Functional Fluids |        |           |
|-----------------------|-------------------|--------|-----------|
|                       | AFF15 (a)         | F1 (b) | AFF16 (c) |
| Siloxane diol DP=8    | 83.07             | 87.97  | --        |
| AEAPTMS               | 16.93             | --     | 59.84     |
| MTM                   | --                | 12.03  | 40.16     |

GLC analysis of the functional fluids showed that (b) the MTM and siloxane diol did not react. Three formulations were prepared, each utilizing one of the functional fluids were evaluated.

For each formulation, 200 parts of a hydroxy-endblocked PDMS polymer having a viscosity of 50 Pa · s at 25°C., 4 parts of Tergitol® TMN-6 surfactant and 4 parts of DI water were charged to 350 ml Whip Mix™ mixers and the mixtures stirred for 30 seconds under vacuum. To these high solids emulsions were added 50 parts of DI water in five increments of 10 parts each, with 30 seconds of stirring between additions. To these dilute emulsions, either 1.8 parts AFF15 (a), 1.7 parts F1 (b) or 0.51 part AFF16 (c), these amounts providing the molar equivalency of 2 parts AFF2, was added as well as 1.6 parts IBTMS and 0.4 part DBTDA and the mixtures were stirred for another 30 seconds under vacuum. The silicone emulsions were packaged and tested for adhesion as described in Example 4. The samples prepared with AFF15 (a) showed cohesive failure to glass, while the samples prepared with F1 (b) or AFF16 (c) failed adhesively to glass. Physical properties of the elastomers are shown in Table 10.

Table 10

| Physical Properties    | Sealant Formulations |          |          |
|------------------------|----------------------|----------|----------|
|                        | S-AFF15              | S-F1     | S-AFF16  |
| Glass Adhesion         | cohesive             | adhesive | adhesive |
| Durometer (Shore A)    | 6                    | 12       | 10       |
| Tensile Strength (MPa) | 0.47                 | 0.65     | 0.55     |
| Maximum Elongation (%) | 1600                 | 880      | 1,280    |

To determine the stability of the various functional fluids, 15 g samples of each fluid were placed in polyethylene bottles, purged with nitrogen, and stored in a 50°C. oven. AFF15, the aminofunctional siloxane prepared without MTM gelled within 4 weeks of storage. No gelation occurred with F1 and AFF16 over the same storage period.

#### Example 11

Aminofunctional siloxanes were prepared by cold blending a siloxane diol with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C., MTM and a functional organosilane in a polyethylene vessel and allowing the mixture to react for 24 hours. The following functional organosilanes were used (a) AEAPTMS, (b) gamma-glycidoxypopyl trimethoxysilane (GPTMS), (c) gamma-methacryloxypropyl trimethoxysilane (MAPTMS) and (d) gamma-mercaptopropyl trimethoxysilane (MPTMS). The various functional organosilanes were added into the cold blend at a constant molar ratio. Table 11 shows the composition of the various functional fluids.

Table 11

| Components (in parts) | Functional Fluids |        |        |        |
|-----------------------|-------------------|--------|--------|--------|
|                       | AFF2 (a)          | F2 (b) | F3 (c) | F4 (d) |
| Siloxane diol DP=8    | 74.6              | 74.6   | 74.6   | 74.6   |
| AEAPTMS               | 15.2              | --     | --     | --     |
| GPTMS                 | --                | 16.2   | --     | --     |
| MAPTMS                | --                | --     | 17     | --     |
| MPTMS                 | --                | --     | --     | 13.4   |
| MTM                   | 10.2              | 10.2   | 10.2   | 10.2   |

Each of these functional fluids were evaluated in elastomer formulations. The addition level of functional fluids to the silicone latex formulation was kept constant at 1 part based on 100 parts of PDMS polymer. The formulations were prepared, packaged and tested as described in Example 4. The samples prepared with AFF2 (a) showed cohesive failure to glass, while the samples prepared with F2 (b), F3 (c) or F4 (d) showed adhesive failure to glass.

#### Example 12

Aminofunctional siloxanes were prepared by cold blending AEAPTMS, MTM and a hydroxy-endblocked organosiloxane in a polyethylene vessel. The following siloxane diols were used: (a) a PDMS organosiloxane with a DP of 7 to 9 and a viscosity of 0.04 Pa · s at 25°C. as described in Example 1, (b) polyphenylmethylsiloxane organosiloxane with an average DP of 5-7 and an average -OH content of 6.55%, and (c) polytrifluoropropylmethyl organosiloxane with an average DP of 5-7 and an average -OH content of 6.10%. The mixtures were allowed to react for 24 hr, after which time 100% of the -OH functionality of the hydroxy-endblocked organosiloxane had disappeared as determined by GLC. Table 12 shows the compositions of the various aminofunctional siloxanes prepared.



Table 12

| Components (in parts)              | Aminofunctional Siloxanes |       |       |
|------------------------------------|---------------------------|-------|-------|
|                                    | AFF2                      | AFF17 | AFF18 |
| Dimethylsiloxane diol              | 74.6                      | --    | --    |
| Phenylmethylsiloxane diol          | --                        | 64.77 | --    |
| Trifluoropropylmethylsiloxane diol | --                        | --    | 66.38 |
| AEAPTMS                            | 15.2                      | 21.08 | 20.12 |
| MTM                                | 10.2                      | 14.05 | 13.5  |

Each of these aminofunctional siloxanes were evaluated in elastomer formulations. The addition level of aminofunctional siloxane to the formulation was kept constant at 1 part based on 100 parts of PDMS polymer. The formulations were prepared, packaged and tested as described in Example 4. The sealant sample prepared with AFF2 (a) showed cohesive failure to glass, wood and concrete and mixed failure mode (50% cohesive) on mill finished aluminum. The samples prepared with AFF17 or AFF18 showed adhesive failure to glass and mill finished aluminum, and cohesive failure to wood and concrete. The physical properties of all samples were quite comparable with durometers being in the 4-5 Shore A range, tensile strengths ranging from 0.34 to 0.37 MPa, and maximum elongations ranging from 2060% to 2300%.

#### Example 13

(a) To demonstrate the stability of a premixture consisting of an aminofunctional siloxane (AFF2), IBTMS, hydroxy-endblocked diorganosiloxane polymer and DBTDA, the following experiment was undertaken. The premixture was prepared as follows: 5000 parts of an hydroxy-endblocked PDMS polymer having a viscosity of 50 Pa · s at 25°C. and 50 parts of AFF2 were charged to a 10 liter Turello™ mixer. The mixture was stirred for 30 seconds under vacuum. To this mixture 40 parts of IBTMS and 3 parts of DBTDA were added and the mixture was stirred for another 30 seconds under vacuum. The viscosity of the mixture was monitored and no significant increase in viscosity was observed over a period of four hours. 104 g samples of this premixture were taken at 60 minute intervals and charged to a 350 ml Whip Mix™ Mixer. To each of these samples, 2 parts of Tergitol® TMN-6 surfactant and 2 parts DI water were added and the mixture stirred for 30 seconds under vacuum yielding a slightly translucent, non flowable, high solids oil-in-water emulsion. DI water was then added in four increments of 4 parts each with 30 seconds of stirring under vacuum between additions. The samples taken from premixture after 1, 2, 3 and 4 hours emulsified without any problems, and the resulting elastomers showed cohesive failure on glass.

(b) Another experiment was performed to evaluate how long after emulsification the aminofunctional siloxane could be added. 5000 parts of an hydroxy-endblocked PDMS polymer having a viscosity of 50 Pa · s at 25°C., 40 parts of IBTMS and 3 parts of DBTDA were added and the mixture was stirred for 30 seconds under vacuum. To this mixture was added 100 parts of Tergitol® TMN-6 and the mixture stirred another 30 seconds under vacuum. 150 parts of DI water was then added and the mixture stirred for 5 minutes under vacuum yielding a slightly translucent, non flowable, high solids oil-in-water emulsion. 106 g samples of this silicone latex dispersion were taken in regular intervals of 60 minutes. The samples were charged to a 350 ml Whip Mix™ Mixer and 1 part of AFF2 was added. The mixture was then stirred under vacuum for 30 seconds. To this high solids silicone emulsion, DI water was added in four increments of 4 parts each with 30 seconds of stirring under vacuum between additions. It was found that the aminofunctional siloxane could be added up to 8 hours (inclusive after emulsification of all other components and still provide cohesive failure mode of the cured sealant to glass.

#### Example 14

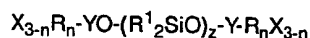
95.67 parts of a hydroxy-endblocked PDMS polymer having a viscosity of 50 Pa · s at 25°C., and 0.06 part of DBTDA were charged to a 350 ml Whip Mix™ pot and the mixture was stirred for 30 seconds under vacuum. To this mixture was added 0.93 part of AFF2 and the mixture was stirred for another 30 seconds under vacuum. 0.08 part of glacial acetic acid were then added and this mixture was stirred for another 30 seconds under vacuum. To this mixture were added 0.70 part IBTMS and the mixture was stirred for another 30 seconds under vacuum. To this mixture were added 2.06 parts of Tergitol® TMN-6 and 2.32 parts of DI water, and the mixture was stirred for another 30 seconds

under vacuum, yielding a slightly translucent, non flowable, high solids oil-in-water emulsion. To this mixture were added 66.28 parts of a 70% solids dispersion of kaolin clay in water and 44.9 parts of a 62% solids dispersion of rutile titanium dioxide in water and the mixture was stirred for another 30 seconds under vacuum. The silicone emulsion was packaged into a Semco<sup>®</sup> cartridge and centrifuged to remove any trapped air. After aging the emulsion for 18 hours at room temperature, a sample was tooled into a 2.54 mm [100 mils] thick film and allowed to cure under laboratory conditions for 14 days. The silicone elastomer had a tensile strength of 0.64 MPa (92 psi), a maximum elongation of 640%, and a Shore A durometer of 22. Further samples of the 18 hour aged silicone emulsion were tooled as 50 mm long and 18 mm wide beads onto glass, concrete, painted pine and red wood as substrates and allowed to cure under laboratory conditions for 14 days. The elastomer exhibited excellent adhesion (cohesive failure mode) to all substrates.

## Claims

1. An aqueous silicone emulsion which forms a silicone elastomer upon the removal of water having improved adhesion to substrates, the silicone emulsion comprising the product formed by mixing:

(A) a diorganosiloxane polymer (I) having the general formula



where

n is 0, 1, 2 or 3,

z is an integer from 200 to 10,000,

X is a hydroxyl group or any hydrolyzable group,

R is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms,

R<sup>1</sup> is individually selected from X groups or R groups, provided that at least 90% of the R<sup>1</sup> groups are R groups, and

Y is a Si atom, a -Si-(CH<sub>2</sub>)<sub>m</sub>SiR<sup>1</sup><sub>2</sub>- group or a -Si-(CH<sub>2</sub>)<sub>m</sub>SiR<sup>1</sup><sub>2</sub>-O-SiR<sup>1</sup><sub>2</sub>-(CH<sub>2</sub>)<sub>m</sub>SiR<sup>1</sup><sub>2</sub>- group, where R<sup>1</sup> is defined above and m is a positive integer;

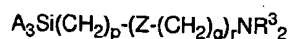
(B) water;

(C) a surfactant;

(D) optionally, a crosslinker;

(E) a tin condensation catalyst;

(F) an effective amount of an aminofunctional siloxane which is formed by reacting components comprising an aminofunctional silane (II) having the formula



where, A is a hydrolyzable group, Z is an oxygen atom or NR<sup>2</sup>, where R<sup>2</sup> is individually selected from hydrogen atom and substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms, R<sup>3</sup> is individually selected from hydrogen atom and substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms, p and q are each a positive integer from 2 to 10 and r is a positive integer from 0 to 3; and a hydroxy-endblocked organosiloxane (III) having the formula HO-(SiR<sup>4</sup><sub>2</sub>)<sub>b</sub>-OH where R<sup>4</sup> is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms and b is a positive integer from 4 to 80; and

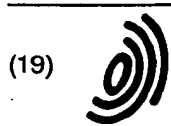
(G) optionally, an acid.

2. The silicone emulsion of Claim 1, wherein the components of the aminofunctional siloxane further comprise a silane (IV) having the formula R<sup>5</sup><sub>c</sub>SiG<sub>4-c</sub>, where R<sup>5</sup> is individually selected from substituted or unsubstituted monovalent hydrocarbon radicals having from 1-15 carbon atoms, G is a hydrolyzable group and c is 0, 1 or 2.
3. The silicone emulsion of Claim 1, comprising 100 parts by weight diorganosiloxane polymer; 8 to 1000 parts by weight of water; 0.1 to 10 parts by weight of surfactant; 0.01 to 5 parts by weight of tin condensation catalyst and from 0.1 to 10 parts by weight of aminofunctional siloxane provided that there is at least 0.0005 part by weight of aminofunctionality and provided further that the molar ratio of component (II) to component (III) is at least 1.
4. The silicone emulsion of claim 1 wherein R and R<sup>1</sup> are each methyl radicals, Y is Si, n is 0, 1 or 2, X is hydroxyl,

methoxy or ethoxy; the surfactant is selected from the group consisting of anionic surfactants, nonionic surfactants and mixtures thereof; the tin condensation catalyst is a stannic tin (IV) compound; and comprising 0.1 to 50 parts of a silane crosslinker having at least 3 alkoxy groups and 0.05 to 0.3 parts by weight of an organic acid.

- 5 5. The silicone emulsion of claim 4 wherein n is 2 and X is hydroxyl; and comprising 15 to 50 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, of water; 0.05 to 5 parts by weight based on 100 parts by weight diorganosiloxane polymer, of a surfactant selected from nonionic or mixtures of nonionic and anionic surfactants; 1 to 10 parts by weight, based on 100 parts by weight diorganosiloxane polymer, of the alkoxysilane crosslinker wherein each alkoxy group has up to 8 carbon atoms; 0.05 to 2 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, of a tin (IV) carboxylate catalyst; the aminofunctional siloxane which is formed by reacting components comprising the aminofunctional silane (II), where A is an alkoxy group, Z is  $\text{NR}^2$  where  $\text{R}^2$  and  $\text{R}^3$  are hydrogen atoms, p and q are each integers from 2 to 6 and r is an integer from 0 to 2, the hydroxy-end-blocked organosiloxane (III), where  $\text{R}^4$  is methyl and b is 4 to 50 and silane (IV) where  $\text{R}^5$  is a methyl group, c is 0 or 1 and G is an alkoxy group; and 0.06 to 0.2 parts by weight based on 100 parts by weight of diorganosiloxane polymer of a carboxylic acid.
- 10
- 15
6. The silicone emulsion of claim 5 wherein the alkoxy groups of A have up to 8 carbon atoms and G is a methoxy or ethoxy group.
- 20 7. The silicone emulsion of claim 5 comprising 1.5 to 5 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, of a polyoxyalkylene alkyl ether surfactant; 2 to 5 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, of the alkoxysilane crosslinker wherein each alkoxy group has up to 3 carbon atoms; 0.06 to 0.5 parts by weight, based on 100 parts by weight of diorganosiloxane polymer, of a dibutyltindiacetate catalyst; the aminofunctional siloxane which is formed by reacting components comprising the aminofunctional silane (II) where in A each alkoxy group has up to 3 carbon atoms, p is 3, q is 2 and r is 0 or 1, the hydroxy-endblocked organosiloxane (III), where b is 6 to 20 and silane (IV) where c is 1 and G is a methoxy group provided that there is at least 0.005 part by weight of aminofunctionality, based on 100 parts by weight of diorganosiloxane polymer, and provided further that the molar ratio of component (II) to component (III) is 0.2 to 0.8, the molar ratio of component (IV) to component (III) is 0.2 to 0.8, the molar ratio of component (II) and component (IV) to (III) is at least 1.1 and the molar ratio of (IV) to (II) is between 0 and 2 inclusive; and 0.07 to 0.13 part by weight, based on 100 parts by weight of diorganosiloxane polymer, of acetic acid.
- 25
- 30

**THIS PAGE BLANK (USPTO)**



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 780 421 A3**

(12)

**EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
01.10.1997 Bulletin 1997/40

(51) Int. Cl.<sup>6</sup>: **C08J 3/03**, C08L 83/04  
// C08L83:04

(43) Date of publication A2:  
25.06.1997 Bulletin 1997/26

(21) Application number: 96120674.5

(22) Date of filing: 20.12.1996

(84) Designated Contracting States:  
DE FR GB

(30) Priority: 21.12.1995 US 576114

(71) Applicant: **DOW CORNING CORPORATION**  
Midland, Michigan 48686-0994 (US)

(72) Inventors:  
• **Hill, Michael Philip Louis**  
Midland, Michigan 48640 (US)

• **Tselepis, Arthur James**  
Midland, Michigan 48640 (US)  
• **Wolf, Andreas Thomas Franz**  
Midland, Michigan 48642 (US)

(74) Representative: **Spott, Gottfried, Dr.**  
Patentanwälte  
**Spott, Weinmiller & Partner**  
Sendlinger-Tor-Platz 11  
80336 München (DE)

**(54) Aqueous silicone emulsions forming silicone elastomers adhering to substrates**

(57) This invention relates to an aqueous silicone emulsion which forms a silicone elastomer upon the removal of water having improved adhesion to substrates. The silicone emulsion comprises the product formed by mixing a diorganosiloxane polymer, water, surfactant, optionally a crosslinker, a tin condensation catalyst, optionally an acid and an effective amount of an aminofunctional siloxane which is formed by reacting an aminofunctional silane and a hydroxy-endblocked organosiloxane.

EP 0 780 421 A3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 96 12 0674

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |   |  |
|---|---|---|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim   | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X   | EP 0 572 006 A (WACKER CHEMIE GMBH) 1 December 1993<br>* claims 1,4,5 *<br>* page 3, line 33 - line 45 *<br>* page 6, line 39 - page 7, line 56 *<br>---                            | 1   | C08J3/03<br>C08L83/04<br>//C08L83:04         |
| P,X   | WO 96 08529 A (RHONE POULENC CHIMIE ;CARDINAUD DENIS (FR); FEDER MICHEL (FR); FIS) 21 March 1996<br>* claim 1 *<br>* page 6, line 19 - page 7, line 5 *<br>---                      | 1   |  |
| P,X   | EP 0 739 947 A (DOW CORNING) 30 October 1996<br>* claims 1,8 *<br>* page 7, line 36 - line 52 *<br>* page 8, line 15 - line 22 *<br>---   | 1   |  |
| A   | EP 0 156 970 A (WACKER CHEMIE GMBH) 9 October 1985<br>* claim 1 *<br>---  | 1   |  |
| A   | EP 0 415 254 A (UNION CARBIDE CHEM PLASTIC) 6 March 1991<br>* claim 1 *<br>---  | 1   | TECHNICAL FIELDS<br>SEARCHED (Int.Cl.6)      |
| A   | EP 0 655 475 A (WACKER CHEMIE GMBH) 31 May 1995<br>* claims 1,5-10 *<br>* page 6, line 45 - page 7, line 39 *<br>* page 8, line 1 - line 6 *<br>* page 9, line 7 - line 15 *<br>--- | 1   | C08J<br>C08L<br>C08G                         |
| A   | PATENT ABSTRACTS OF JAPAN<br>vol. 007, no. 161 (C-176), 15 July 1983<br>& JP 58 069250 A (SHINETSU KAGAKU KOGYO KK), 25 April 1983,<br>* abstract *<br>-----                        | 1   |  |
| The present search report has been drawn up for all claims  |   |   |  |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>23 July 1997  | Examiner<br>Depijper, R                      |
| CATEGORY OF CITED DOCUMENTS   |   | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>-----<br>& : member of the same patent family, corresponding document |  |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |   |   |  |

EPO FORM 1503 03.82 (P04C01)